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(54) Title: A METHOD FOR PRODUCING CAST-IRON, AND IN PARTICULAR CAST-IRON WHICH CONTAINS VERMICULAR GRAPHITE

(57) Abstract

Method for producing castings from cast-iron containing structure-modifying additives. A sample from a bath of molten iron is permitted to solidify during 0.5 to 10 minutes. The temperature is recorded simultaneously by two temperature responsive means, one of which is placed in the centre of the sample and the other in the immediate vicinity of the vessel wall. The dispersion degree of the graphite phase is assessed in relation to known reference values by aid of recorded values of supercooling at the vessel wall, the recalescence at the vessel wall, the difference between the temperature at the vessel wall and at the centrum of the vessel and the derivative of the temperature decrease at the vessel wall during the time of constant eutectic growth temperature at the centre. When necessary a graphite nucleating agent is added to the molten bath or the dispersion is lowered by implementing a holding time prior to casting. The morphology of the graphite precipitation is also determined by aid of recorded values and possibly corrected by changing the amount of structure-modifying agents present.

A method for producing cast-iron, and in particular
cast-iron which contains vermicular graphite.

The present invention relates to a method for producing
cast-iron containing structure modifying additives, and
preferably additives which will cause carbon to precipi-
tate in vermicular graphite form.

5

Vermicular graphite is defined as "Form III"-graphite in
ISO/R 945-1969, and alternatively "Type IV"A according to
ASTM Specification A 247.

10   Cast-iron is one of the most essential materials in in-
dustrial casting processes, and upon solidifying may pre-
cipitate carbon in cementite, Fe_3C form, to form white
cast-iron or in graphite form, to form grey cast-iron.
White cast-iron is brittle, but has a high compression

15   strength and is highly resistant to wear. Grey cast-iron
can be readily worked and has an extremely wide field of
use within machine technology. In grey cast-iron graphite
is normally precipitated in flake form. This results in a
cast-iron of limited rupture strain (0.5%). Grey cast-iron

20   has good thermal conductivity, but undergoes permanent
changes in volume at elevated temperatures, which
restricts its use for some purposes. Consequently,
attempts have been made to change the morphology of the
precipitated graphite, by incorporating certain additives.

25   In this respect, magnesium, or magnesium in combination
with rare earth metals like cerium, has normally been
used, these modifying additives preventing the growth of
flaky graphite and resulting in a graphite in the form of
small spheroids or nodules. This material is known as no-

30   dular cast-iron or spheroidal-nodular iron. The use of
nodular iron as a construction material has grown widely
within the construction field. Additional developments

within this field have involved the creation of other gra-
phite morphologies, of which the majority have obtained
but limited technical use. It has been found, however,
that so-called compacted graphite cast-iron, or so-called
5   vermicular iron, has properties which render it of parti-
cular interest, and which give it a superiority over grey
cast-iron and nodular iron in respect of many different
areas of use. Minor deviations from desired additive quan-
tities and the presence of impurities, however, are fac-
10   tors which make it impossible to use cheap raw materials,
and hence manufacture has been restricted to a few foun-
dries which have built-up an expertise by carrying out
large numbers of tests and experiments and by using raw
materials and additives which are well defined through
15   experience and which are often expensive.

There is therefore an obvious need for a method by means
of which preparation of any molten bath of cast-iron mate-
rial can be controlled in a manner to bring the bath to
20   solidify to vermicular iron with a reproduceable result.

In the casting of metals, great importance is placed on
the composition of the molten bath, although the physical
state and other factors influencing the course followed by
25   crystallisation of the bath-constituents are also factors
of decisive importance with respect to the final proper-
ties of the end product.

The chemical composition of the bath, such as alloying
30   elements, impurities, gas content, etc., can be quickly
monitored and checked with the aid of modern analysis
apparatus, enabling necessary corrections to be made.

On the other hand, however, no method has yet been fully

developed by means of which it is possible to predict and
control swiftly and reliably the nature of the crystal
structure which a given bath of molten material will
obtain upon solidifying under prevailing solidification
5   conditions, even though many experiments and tests carried
out to this end are found described in the relevant lit -
rature, and many patent applications relating to such
methods have been filed.

10   Casting materials can be divided into two main groups,
depending on the nature of the solidification process, of
which main groups the first includes material which soli-
dify in a single phase (primary solidification processes).
This group incorporates most types of steel, aluminium
15   alloys and copper alloys. The other group incorporates
materials which solidify in two or more phases (secondary
solidification processes). Examples of materials belonging
to this group are various types of cast-iron silumin-type
aluminium alloys (Al, 8-12 % Si).
20

Accordingly, the object of the present invention is to
provide a method for controlling secondary solidification
processes, primarily in the solidification of molten cast-
iron, so as to obtain compacted graphite cast-iron or ver-
25   micular cast-iron from starting materials comprising con-
ventional, readily available iron raw materials and steel
scrap, which has not previously been possible.

To this end there is used a thermal analysis technique in
30   which the temperature prevailing in various parts of a
sample taken from the molten bath in question is measured
and recorded in dependence of time.

This temperature-time recording technique is not novel per
35   se, but is a classic method of determining conversion tem-

peratures and fusion temperatures. Crystalline conversion
normally takes place at given temperatures or within given
temperature ranges.

5   In such techniques, a temperature responsive device, such
    as a thermometer, a thermoelement, a thermistor or the
    like, is located in or placed in contact with a sample or
    test vessel, which is heated or allowed to cool in accor-
    dance with a set program. The conversion temperature is
10 recorded, as is optionally also the derivative of a soli-
    dification curve, or the difference measured between
    corresponding values for a known reference material.

    The method has been used within the field of metallurgy to
15 carry out rapid chemical analyses, for example to deter-
    mine the so-called carbon equivalent

    $$(CE = \text{total carbon content in percent} + \frac{\% \text{ Si} + \% \text{ P}}{3})$$

20 in cast-iron, by pouring a sample of the bath into a foun-
    dry-sand sample beaker having a thermoelement placed cen-
    trally therein. When iron crystals (austenite) form from
    the molten material, a plateau can be read-off from the
    solidification curve, this plateau disclosing the carbon
25 equivalent in accordance with the calibration of the samp-
    ling method applied. Thus, the apparatus conventionally
    used is principally suited for effecting a quick assay of
    the composition of the iron, but reveals nothing with res-
    pect to the possible crystalline form of the austenite
30 formed. Such apparatus is sold, inter alia, by the Ameri-
    can company Leeds & Northrup under the trade mane "TECTIP".

    Similar apparatus have also been used to determine the
    eutectic growth temperature in the iron-carbon-silicon-
35 system, and for determinating the extent of supercooling

prior to the eutectic reaction. The measuring results
obtained herewith, however, give no satisfactory indica-
tion of the crystalline structure which can be expected
upon solidification of the molten bath and during the
5   aforesaid eutectic reaction. In apparatus such as these in
which the molten material is poured into a cold mold,
there is namely formed momentarily a skin of solid phase
close to the cold wall of the mold, where iron with a gra-
phite phase and iron with a carbide phase occur, and at
10   the relevant growth temperatures for respective phases the
said phases are able, quite simply, to grow without having
reached supercooling critical to effect new or renewed
nucleation.

15   A critical review of the usefulness of this method in res-
pect of nodular cast-iron has recently been published in
AFS Transactions 82:131, pages 307-311. This review shows
that reliability in accuracy afforded by this method in
determining structures lies at a confidence level of 80 %,
20   which is quite unsatisfactory with regard to commercial
production methods.

Still worse results can be expected when attempting to
prophecy the formation of vermicular graphite, which
25   requires the measuring method to be far more accurate.

These fundamental deficiencies in current thermal analysis
techniques, have, however, been partially overcome by the
technique described in Swedish Patent Specification No.
30   350 606.

With this technique it is possible to measure factual
supercooling and growth temperatures during the formation
and growth of crystals, by immersing the sampling vessel
35   in the molten bath or heating the vessel in some other
way, so that both the sampling vessel and its contents
have reached thermal equilibrium at a temperature above

the temperature of crystallisation prior to commencement
of the cooling process. An improved indication of the
various crystalline growth fenomena during the process of
solidification can be had by measuring the supercooling
temperature prior to nucleation, recalescence (re-heating
by released heat of crystallisation) strength and duration
(represented simplest by the maximum value and duration of
the positive derivative). An essential problem remains,
however, when measuring the eutectic reaction of cast-
iron; the recalescence function and growth temperature are
not solely contingent on the growth form, but also on the
concentration of the graphite crystals formed (= number of
graphite crystals per unit volume) and the method allows
no distinction between these two factors, such distinction
being necessary in order to predict the structural
formation and to enable the process to be influenced in
the right direction.

It is possible to determine other properties of the soli-
dified material, for example the dimensional change (with
dilatometry) or the thermal conductivity in a fully soli-
dified sample, about $100^{\circ}C$ beneath the solidifying tem-
perature, (Swedish Patent Application No. 7805633-0). It
is not possible, however, with the aid of these methods to
determine structural formation with sufficient accuracy,
either with respect to morphology or with respect to the
degree of dispersion of the graphite phase.

It is now possible as a result of the present invention to
establish reliably the structural formation of a solidi-
fying bath during the actual solidification process, by
applying a newly developed technique based on thermal ana-
lysis. According to this novel technique, a sample quan-
tity taken from the molten bath in question is transferred
to a sampling and testing vessel which is heated to thermal

equilibrium between the vessel and the molten sample
contained therein, at th temperature above the
crystallisation temperature, and a recording is made of
the change in temperature taking place with time at the
5   centre of the sample and at a location immediately
adjacent the wall of the sample vessel. In this way there
are obtained two mutually separate solidification curves
which are able to provide more complete information regar-
ding the process of solidification during casting. (Here-
10   inafter reference is made solely to a sample vessel,
although it will be understood that by this is also meant
a test vessel.)

The present invention relates to a method for producing
15   castings from a cast-iron melts containing structure modi-
fying additives, characterized by producing an initial
cast-iron bath; removing a sample quantity of the bath
with the aid of a sampling vessel; causing the sample
quantity to solidify from a state in which the sampling
20   vessel and the sample quantity are substantially in ther-
mal equilibrium at a temperature above the crystallisation
temperature of the bath; and allowing the sample quantity
to solidify fully over a period of from 0.5 to 10 minutes,
the temperature-time-sequence being measured and recorded
25   simultaneously by two temperature responsive means, of
which one is placed in the centre of the sample quantity
and the other in the molten material closely adjacent the
wall of the sampling vessel. The degree of dispersion of
the graphite phase in relation to known reference values
30   for the same sampling process is assessed with the aid of
the temperature measured during the first crystallization
events in the molten material at the vessel wall, the
recalescence at the vessel wall (rek_v), the positive
difference between the temperature at said wall and in the

centre of the sample quantity ($\Delta T+$), and the temperature gradient in the sample behind the eutectic growth front expressed as ($\frac{dT}{dt}$) ($T_c$max) (approximately constant at least for a short period during the eutectic growth in

5   the centre of the sample quantity ($\frac{dT}{d\tau}$)$_c$ = 0)

optionally expressed as the greatest negative values (ΔT_{max}) of the temperature difference, wherewith in the

10   event that the molten bath has an insufficiency of crystallisation nuclei a graphite nucleating agent is introduced thereinto, and conversely when it is found that the crystallisation nucleants are in excess, this excess is reduced. The morphology of graphite precipitation is

15   determined in relation to known reference values for the same sampling process, with the aid of the crystallisation temperature at the centre of the bath (T^*_c), the recalescence at the centre (rek_c) and the maximum growth temperature ($T_c$max), and the quantity of structure modi-

20   fying agent present is corrected so that graphite is precipitated in a vermicular form during solidification of the cast-iron melt after casting.

The invention will now be described in more detail with

25   reference to the accompanying drawings, in which

Figure 1 is a graphic presentation of a solidification diagram derived from measurement values obtained when producing vermicular cast-iron and

30

Figures 2,3 and 4 illustrate various exemplary embodiments of sampling vessels appropriate for use when practising the method according to the present invention.

Fig. 1 thus shows temperature (T)-time (τ)-curves of which
curve I represents the course of solidification at a loca-
tion close to the wall of the sampling vessel, and curve
II represents the course of solidification at the centre
5   of the sample in the vessel.

Referring to both curves, reference 1 indicates the point
at which there is a fall in the temperature decrease per
unit of time due to heat generated by the formation of the
10 primary phase austenite. The reference 2 on curve II illu-
strates the point at which austenite crystals (in dendri-
tic (branched) form) have formed throughout the whole of
the sample quantity. Subsequent hereto, the molten sample
material is enriched between the austenite crystals with
15 carbon (and other alloying elements) so that gradually, as
the decrease in sample temperature continues, the eutectic
composition is reached.

The reference 3 on curve I indicates the point at which
20 the temperature drop terminates. Graphite crystals are
formed at the vessel wall with sufficient supercooling,
and these graphite crystals grow together with the iron
phase in an eutectic mixture. After this stage in the
solidification process, the molten sample is re-heated
25 (through recalescence) towards the equilibrium temperature
of the eutectic mixture. This is marked with a broken line
T_{Eu} in Fig. 1. At this early stage of the eutectic reac-
tion, however, a steady state in the growth in relation
with growth inhibiting mechanisms has still not been fully
30 reached and the rate at which recalescence takes place
therefore denotes substantially the number of active gra-
phite nuclei per unit of volume. Similarly, the reference
4 in curve II indicates the point of maximum supercooling,
T^{*}_{c}; 6 indicates the recalescence curve; and 7 indicates
35 the current growth temperature at steady state in the cen-

tre of the sampling vessel. These values provide informa-
tion relating to the growth mechanism at the state of
eutectic solidification.

5   The temperature at the wall can be said to represent a
"momentary image" of the course of crystallisation in a
restricted volume of molten material (thin wall) and the
temperature in the centre of the vessel represents an
"integrated" image of the thermal behaviour throughout the
10   whole of the interior of the sample. The temperature along
the radius in the sample quantity between the two measu-
ring locations will include a temperature wave which pro-
pagates forwardly and reflects the growth sequence along
an inwardly advancing eutectic solidification front. This
15   means in practice that the outer thermoelement registers a
solidification process corresponding to that in thinwalled
castings, while the central thermoelement provides infor-
mation concerning the solidification sequence in thicker
parts of the casting. Only when possessing this combined
20   information is it possible to draw conclusions concerning
the ability of a molten material to form a desired struc-
ture in castings of varying thickness during a casting and
solidifying process.

25   This description of the solidification process is mainly
related to hyper-eutectiod cast-iron compositions. The
method can also be applied, however, to cast-iron of
eutectic and hyper-eutectic composition. Primary crystal
growth does not occur upon the solidification of a eutec-
30   tic composition, and will only occur with respect to a
primary graphite precipitation in the case of hyper-
eutectic compositions.

It has been found experimentally that when insufficient
35   supercooling, weak recalescence and high growth tempera-

ture prevail during the solidification process, a flaky
graphite is formed.

On the other hand, if a high supercooling temperature,
5 small recalescence and low growth temperature prevail,
this signifies that the graphite will solidify in a
nodular form and that nodular cast-iron, or spheroidal
nodular iron, will be obtained.

10 When vermicular graphite is disassociated during solidi-
fication, there is obtained a high supercooling, a strong
recalescence and a high growth temperature.

The deviations exhibited by the curves are sufficiently
15 pronounced to permit a fine graduation to be made within
these main groups, and it is thereby possible to predict
the formation of vermicular graphite with a high degree of
certainty, which in turn enables the process to be con-
trolled to within fine limits.
20
Assuming that external conditions remain the same from
case to case, it is possible to make comparisons between
the two values recorded by the temperature responsive
means located adjacent the wall of the sampling vessel and
25 in the centre of the molten sample quantity and between
different tests on the molten bath. It is, of course,
necessary that differences in technique and the geometry
of the sampling vessel and the material located therein
are so small that reproduceable and comparable results can
30 be obtained from different samples.

A number of sampling vessels suitable for use when carry-
ing out the solidification test will be described herein-
after with reference to Figs. 2-4. The methodology app-
35 lied, must, of course, be the same with each sample or

12

test, such that temperature equilibrium is achieved
between molten material and sampling vessel. The tempera-
ture around the sampling vessel is regulated so that heat
is lost from the sampling vessel in a manner which enables
5   the molten material to solidify over a period of 0.5-10
minutes. The lower limit is governed by the fact that more
rapid cooling results in the formation of cementite in
accordance with the metastable system. Slower cooling than
10 minutes is impractical from the aspect of production
10   and, morever, the accuracy of the measuring results
obtained is impaired by other reactions taking place in
and around the vessel and by convection. An ideal cooling
period is from 2 to 4 minutes. The dimensions of the
sampling or testing vessel are not so critical, although
15   for practical reasons the diameter of the vessel should
not be smaller than about 2 cm or greater than about 10
cm. A suitable diameter is from 3 to 6 cm, and it will be
understood that the vessel is suitably filled to a height
of some centimeters and that the height of the fill of the
20   sample must be greater than its diameter. It is preferably
ensured that heat is lost from the sampling vessel in
essentially a radial direction. This can be achieved by
insulating the upper and lower surfaces of the sample
quantity.
25

Although the sampling technique applied may vary from
series to series, it must, of course, be the same within a
particular sample series to be compared. When sampling the
molten bath material, the sampling vessel may, for exam-
30   ple, be immersed in the molten bath and held there until
it is heated to the temperature of the bath. Alternative-
ly, the sampling vessel may be pre-heated to bath tempera-
ture and then fill d with molten bath material, while
another suitable method is one in which the test vessel
35   and the molten sample contained therein are placed in a

separate oven or kiln prior to recording the solidifica-
tion curve, and there heated to equilibrium. Repeated
tests can be carried out, by immersing a sampling vessel
into the molten bath and recording the solidification cur-
5   ve of the sample taken, and then re-immersing the vessel,
together with the solidified sample, into the bath, so
that the solidified sample is re-smelted and the vessel
refilled with a fresh sample.

10 The release of latent heat and the eutectic growth front
(which is dependent on the pertinent growth mechanism) and
the thermal conductivity of the solidified layer behind
the front are highly dependent on both the number of gra-
phite crystals in the eutectic structure and the form of
15 said crystals. A suitable method of determining this com-
posite function is obtained by determining the slope
$(\frac{dT}{d\tau})$ obtained during solidification through the agency
of the temperature responsive means located adjacent the
vessel wall over that period of time during which the
20 temperature responsive means located in the centre of the
vessel records a plateau temperature (corresponding to the
temperature at eutectic steady state $T_c max$, a time
period over which $(\frac{dT}{d\tau})_c$ is thus equal to zero. This
composite function can also be determined by measuring the
25 maximum difference (ΔT_{max}) between the two curves during
the process of solidification. It is found that the values
change for different graphite forms in the cast-iron in
both cases. Grey cast-iron comprising flaky graphite pro-
duces but small temperature differences between the two
30 solidification curves. Nodular iron produces large values
of ΔT_{max}, whereas cast-iron solidifying to vermicular
iron produces values therebetween, therewith providing
splendid possibilities for differential assessment of the
solidifying properties of respective molten baths.

At the eutectoid transition (in solid phase from austenite
to ferrite and cementite (point 8) the rate, and therewith
the final structure, can be followed in detail by compa-
ring deviations from the two measuring points, and parti-
5   cularly by comparing the time displacement and magnitude
of the derivated functions.

In addition to the aforedescribed possibility of recording
double solidification curves from an unknown sample and
10   comparing the configuration of these curves with corres-
ponding curves obtained from samples of known crystalli-
sing characteristics (either graphically or in some other
recording medium, such as a data processor), the following
properties are characteristic when producing cast-iron
15   containing graphite which solidifies to vermicular form.

The most reliable method of ascertaining the vermicular
growth form is to utilize to this end the supercooling in
the centre (T^*_c), the recalenscence sequence (rek_c)
20   and the eutectic maximum growth temperature ($T_c max$).

The actual degree of dispersion (here defined as the num-
ber of graphite crystals/unit volume) can be determined by
the recalescence sequence at the wall (rek_v), ΔT_{max} or
25   alternatively ($\frac{dT}{d\tau}$)$_v$ at $T_c max$ through the temperature
curve of the first eutectic nucleation events. The first
nucleation events are normally encountered as the degree
of supercooling, T^*_v, but in the case of very effective
graphite nucleation an arrest in the cooling curves
30   indicates the formation of small amounts of flaky graphite.

All of the magnitudes recited here can be measured with a
precision and reproduceability which enables the inherent
crystallisation properties of the molten bath to be asses-
35   sed.

It is not always necessary to use all of the aforesaid
variables, since these variables are interrelated, as will
be evident from the aforegoing, and consequently in a

5   well-calibrated system it is sufficient to use only a few
of said variables, and in certain cases solely one or the
other of said variables, in order to determine the
crystallisation properties of an individual molten bath.
In systems such as these it is possible to obtain the

10   major part of the relevant information from a single
eccentrically located thermoresponsive means.

One skilled in foundry technique is well able to determine
which of the suggested data shall be chosen for practical

15   production of a stable vermicular cast-iron and in which
manner the measuring data shall be recorded and evaluated.
Naturally, the simplest method is to compare calibrated
standard curves with recorded curves based on the measu-
ring values obtained, although these values can also be

20   compared in digital form through automatic data processing.

For the purpose of clarifying these various possibilities,
Fig. 1 illustrates graphically curves in which time τ is
plotted against the difference between the two curves;

25   curve I minus curve II = ΔT, and where the region of the
positive ΔT-values is illustrated by a hatched region,
and finally ($\frac{dT}{d\tau}$) has been drawn for the two curves, whe-
re the aforesaid values are illustrated in derivated form,
rek_v and rek_c being shown as hatched areas of positive

30   value.

Thus, it is possible to read from the graphic curve those
measures which should be taken in order to obtain a desi-
red result, and then to show that the desired result has

35   been achieved, optionally by taking further samples and
carrying out further tests. Knowledge of the crystallisa-

tion properties of the molten bath enables necessary additions or necessary removal of relevant substances to be made, and it also lies within the expertise of one skilled in the art to measure the crystallisation properties fully

5   automatically and then correct automatically the composition of the molten bath with the aid of data-programming techniques, so as to obtain vermicular cast-iron. The rate of solidification will be dependent on the thermal conductivity of the vessel wall, the wall thickness, the volume-

10 surface-ratio of the sample and the ambient temperature. Although all of these parameters can be varied, it will be understood that they must be adapted to enable the sampling or testing method to be carried out in a practical manner and be adapted for intended castings of

15 various dimensions.

The sampling vessel is cooled most simply in atmospheric air at ambient temperature, although it may also be convenient to prolong the course of solidification, by causing

20 solidification to take place in an oven at a temperature between the melting point of cast-iron and the ambient temperature. The solidification time can also be extended by isolating the sampling vessel, or by placing the vessel in an insulating jacket during the solidification process.

25 If desired, the solidification process can also be accelerated with cooling air, dim-spray or some similar expedient. It is not possible to describe in general terms the form which a sampling device shall take, although it lies within the expertise of one skilled in this art to devise

30 the sampling and testing method in a manner to achieve the conditions recited in the following claims.

Prior to commencing the measuring process, the entire arrangement, sampling vessel, temperature chamber and the

35 molten material present therein must be substantially in

thermal equilibrium at a temperature above the melting point of the sample. This represents a temperature of about 1200-1400°C in the case of cast-iron.

5   This state of equilibrium can be reached, for example, by constructing the sampling vessel together with the temperature responsive means in a manner which will enable them to be immersed in a molten bath heated to a temperature of about 1200-1400°C and held in the bath until the whole
10   arrangement is heated to this temperature, and then removed from the bath and allowed to cool. The temperature responsive means are therewith connected to some form of recording device, which stores measuring data in analogue or digital form.
15
It will therefore be understood that the sampling or testing vessel can be constructed in different ways, and three embodiments of suitable sampling or testing vessels are illustrated in Figs. 2-4.
20
Fig. 2 illustrates an embodiment of a suitable sampling or testing vessel for immersion into a hot molten bath, said vessel comprising a sleeve 1 of heat resistant material, suitably a ceramic material. The sleeve 1 is attached to a
25   tubular member 2 by means of which the vessel can be held and immersed into the bath. The sleeve 1 is provided with an opening 3 through which molten material can flow into the sleeve. Arranged in the sleeve 1 are two thermoelements 4 and 5, one being placed in the immediate vicinity
30   of the sleeve wall 4 and the other in the centre 5 of the sleeve. The thermoelements are connected to a recording device (not shown) by conductors 6.

Fig. 3 illustrates another embodiment of a sampling or
35   testing vess 1 which can be filled with hot bath material

●

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for the purpose of making an analysis. The vessel of this
embodiment comprises a sleeve 7 having temperature respon-
sive means 8 and 9 inserted through the bottom thereof,
the one (8) of said temperature responsive means being
5   placed adjacent the sleeve wall, and the other (9) being
placed in the centre of the sleeve. The vessel is surroun-
ded by heating coils 10 for pre-heating the vessel. The
temperature responsive means 8 and 9 are connected to
recording devices (not shown) by means of conductors 11.
10

Fig. 4 illustrates a further embodiment of the sampling or
testing vessel, comprising a sleeve 12 which is surrounded
by a high-frequency heating device 13 for re-heating the
vessel and the sample contained therein. Molten material
15   can be transferred to the vessel with the aid of a ladle.
The sleeve 12 of the this embodiment is arranged to ço-act
with a lid 14 provided with guides 15 for locating the lid
on the sleeve 12, and with downwardly extending
temperature-responsive means 16 and 17, which are connec-
20   ted to a recording device (not shown) by means of conduc-
tors 18. The lid, carrying the temperature-responsive
means, is placed on the sleeve 12 subsequent to heating
the vessel and the sample contained therein to the requi-
site temperature.
25

When practising the invention, there is produced a conven-
tional cast-iron molten bath whose chemical composition is
adjusted to desirable values in accordance with chemical
analysis. A sample of the bath is then taken for thermal
30   analysis in accordance with the invention, and the solidi-
fication curves recorded. The inherent nucleating ability
of the molten bath is assessed and any requisite additions
of oxide-sulphide-forming agents are made, in order to
obtain the desired primary nucleating ability. Examples of
35   suitable oxide and sulphide forming additives include cal-

cium, aluminium and magnesium. Another prerequisite for
graphite nucleation is that the carbon equivalent, CE, is
sufficiently high. Consequently, nucleation can be facili-
tated by adding a substance which locally increases the
5   carbon equivalent, CE, such as ferro-silicon quartz or
silicon carbide for example. Although the addition of
nucleating agents is well known within the art, it has not
previously been possible with the aid of known measuring
methods to ascertain with sufficient accuracy the need for
10   making such additions prior to casting.

Subsequent to calibrating the system, particularly impor-
tant information is obtained concerning the nucleating
ability of T^*_v and rek_v and ΔT-function. A deficiency
15   in nucleating agents can result in increased supercooling,
this increase being so great in certain cases that a tran-
sition to the metastable system occurs at the edges of the
sampling vessel. An extremely rapid recalescence takes
place when white cast-iron solidifies. In order to form
20   nodular iron, the formation of nuclei has to be hundreds
of times greater than that required for forming flaky gra-
phite. In order to obtain vermicular iron, the nucleating
ability has to be smaller than that required to form nodu-
lar iron, suitably in the order of magnitude of one tenth.
25   If an excessively low nucleating ability is measured, a
nucleating stimulant can be added, while if it is desired
to lower the nucleating ability the molten bath is simply
allowed to stand for a given period of time, since the
nucleating ability decreases with extended holding times.
30
The quantity of active structure-modified substances is
regulated with respect to supercooling at the centre of
the molten material (T^*c), the recalescence at the centre
of the material (rek_c) and the maximum growth temperatu-
35   re ($T_c max$). When the sample solidifies, the amount of

active structure-modifying substances present will control
the crystal growth. When forming nodular graphite, the
growth is restricted in three directions when graphite
precipitation has reached a certain level, but if the
5   quantity of active structure-modifying substances is redu-
ced slightly in relation to that required to obtained
nodular graphite, crystal growth will be restricted solely
in two directions, leaving the possibility for crystal
growth from the molten metal to take place in the third
10   direction, such crystal growth then taking place to form
worm-like graphite crystals. An analysis of the aforegiven
values (T^*_c, rek_c and $T_c max$) will reveal whether or
not the molten bath contains sufficient structuremodifying
substances. When this content is found to be insufficient,
15   structure modifying elements are added. Magnesium
optionally in combination with rare earth metals, such as
cerium may serve this purpose. An excessively high content
of structure-modifying substances can be rectified by
oxidation, which can be effected by introducing oxygen
20   into the bath, or by adding an oxidising agent, such as
magnetite thereto. Oxidation can also be effected by
exposing the surface of the metal to air for a period of
some minutes. Inhibitors, such as titanium, can also be
added to the bath for the purpose of decreasing the
25   content of active structure-modifying substances.

The present invention is primarily intended to solve the
problem of controlling casting processes to solidification
with vermicular graphite precipitation. Notwithstanding
30   this, however, the method also affords the valuable possi-
bility of accurately determining the dispersion degree
when producing grey cast-iron, and therewith to control
the type of flaky graphite precipitated. It is also possi-
ble to determine accurately the quantity of structure
35   modifying substances and the desired degree of dispersion

when manufacturing spheroidal-nodular iron, thereby enab-
ling savings to be made in the use of expensive additives.

5 Irregularities in the solidification curve obtained when
   measuring the sample in the centre thereof, towards the
   end of the solidification phase, can also show possible
   carbide formation, which in turn provides a valuable indi-
   cation that there is a deficiency in nucleating agent in
   combination with the presence of a carbide stabilizing
10 element, being segregated in the microstructure.

It will also be understood that there is always used
within the foundry technique a well-tried calibration
which is contingent on the local conditions and which in-
15 corporates types and structural configurations of melters
   and optionally devices for melt-treatment, heat-holding
   and casting of the type of castings to be produced. Avail-
   able analysis and measuring methods are used in this work
   to the best possible extent, and the present invention
20 affords herewith a solution to a difficult material-con-
   trol problem prevailing within the foundry industry.

It will be understood, that when controlling the casting
process, a series of mutually different factors can be
25 derived from the solidification curves and the configura-
   tion taken by the curve as a whole can be optionally ana-
   lyzed and compared with the known total process develop-
   ments. Modern data technology enables significant values
   to be taken in algorithms and compared with corresponding
30 reference data, enabling the melt-treatment process to be
   controlled on the basis thereof, optionally in a fully
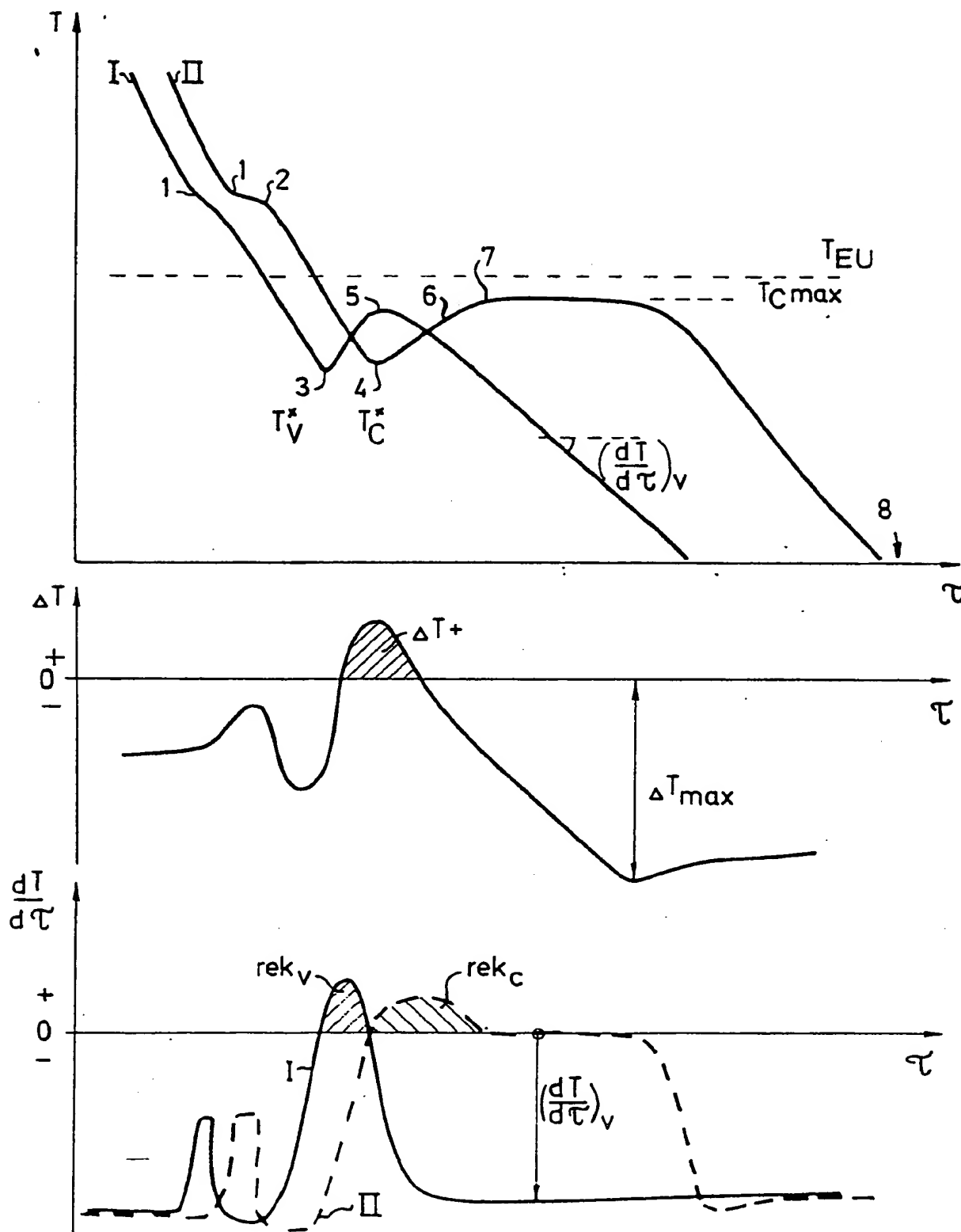   automatized system.

CLAIMS

1. A method for producing castings from cast-iron contai-
ning structure modifying additives, characterized by pre-
paring a molten cast-iron bath; removing a sample quantity
of the bath with the aid of a sampling and testing vessel;
5   causing the sample quantity to solidify from a state in
which the vessel and the sample quantity are substantially
in thermal equilibrium at a temperature above the crystal-
lisation temperature of the bath, and allowing the sample
quantity to solidify fully over a period of from 0.5 to 10
10   minutes, the temperature-time sequence being measured and
recorded simultaneously by two temperature responsive
means, of which one is placed in the centre of the sample
quantity and the other in the molten material at a loca-
tion close to the wall of the vessel; by assessing the
15   degree of dispersion in relation to known reference values
for the same sampling and testing process with respect to
finished castings with the aid of the temperature measured
during the first nucleation events of the eutectic reac-
tion measured at said vessel wall represented by (T^*_v)
20   taking place, the recalescence at the vessel wall (rek_v)
the positive difference between the temperature at the
vessel wall and in the centre $(\Delta T+)$ thereof, and the deri-
vative of the temperature decrease at said vessel wall
during the time for constant eutectic growth temperature
25   $(\frac{dT}{d\tau})_c$ = 0 in the centre of the sample quan-
tity $(\frac{dT}{d\tau})_v$ $(T_c max)$,
alternatively the highest negative values (ΔT_{max}) of the
temperature difference, wherewith in the event that the
bath has an insufficiency of crystallisation nuclei a gra-
30   phite nucleating agent is introduced thereinto, and con-
versely when the crystallisation nucleants are present in
excess the degree of dispersion is lowered by holding the
bath prior to casting; and by assessing the morphology of
the graphite precipitation in relation to known refe-

rence values for mutually the same sampling and testing
method with the aid of supercooling taking place in the
centre (T^*_c) of the molten material, the recalescence in
the centre (rek_c) and the maximum growth temperature

5   ($T_c max$) and correcting the quantity of structure-modi-
fying means in response thereto so that graphite precipi-
tation takes in place a pre-determined form upon solidifi-
cation of the molten cast-iron subsequent to casting.

10   2. A method for producing cast-iron castings according to
Claim 1, characterized in that the bath contents of both
nucleating and structure-modifying agents are controlled
so that the molten cast-iron solidifies with graphite in
vermicular form subsequent to casting, this being achieved

15   by causing the recorded measuring data to coincide with
corresponding data obtained with the same sampling and
testing technique applied with cast-iron of known vermicu-
lar structure.

20   3. A method according to claim 1, characterized in that
the sample is taken from the molten bath by immersing a
sample vessel into the bath and removing said vessel sub-
sequent to filling the same with molten material and hea-
ting said vessel to the temperature of the bath.
25

4. A method according to Claim 1, characterized by remo-
ving a sample from the molten bath and transferring said
sample to a sampling and testing vessel, which is there-
with pre-heated to a temperature approximately equal to

30   the temperature of the molten material prior to the sample
being allowed to solidify.

5. A method according to Claim 1, characterized by remo-
ving a sample from the molten bath and transferring the

sample to a sampling and testing vessel, and by subse-
quently heating the vessel and the molten material contai-
ned therein to a temperature equilibrium corresponding to
the temperature of the molten bath, prior to allowing the
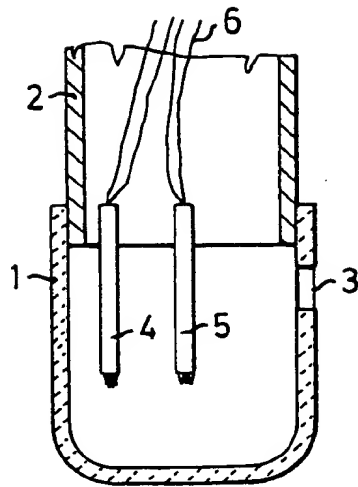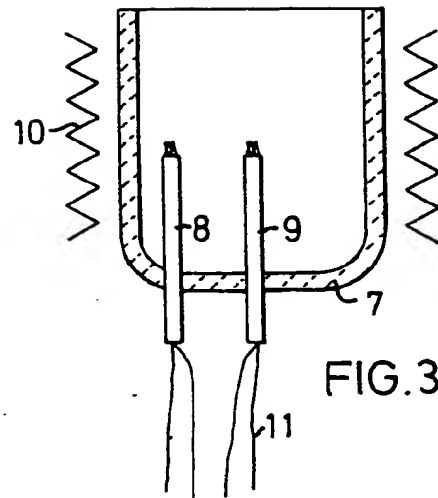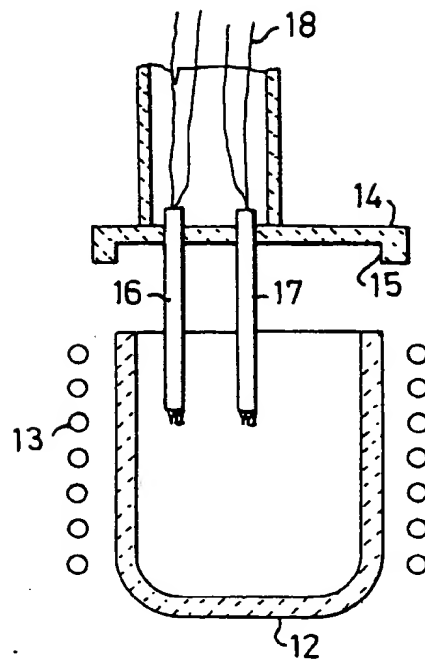5   sample to solidify.

FIG.1

FIG. 2

FIG. 3

FIG. 4

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC 4

B 22 D 2/00, C 21 C 1/08

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC 4	C 21 C 1/00, /08, /10; B 22 D 2/00, 46/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	SE, B, 350 606 (S L BÄCKERUD) 28 October 1971	1
A	SE, A 7805633-0 (ELECTRO-NITE N V) 19 November 1978	1
A	Gjuteriet 62(1972):5 page 6, second and third column	1

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1985-11-20	1985 -12- 0 3
International Searching Authority	Signature of Authorized Officer
Swedish Patent Office	Johan Von Döbeln

Form PCT/ISA/210 (second sheet) (January 1985)

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